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ORGANIC PHOTOCHROMISM

(IUPAC Technical Report)

Prepared for publication by
HENRI BOUAS-LAURENT[1] AND HEINZ DÜRR[2]

[1]*Laboratoire de Chimie Organique et Organométallique, Groupe de Photochimie Organique, CNRS, UMR 5802, Université Bordeaux 1, F-33405 Talence Cedex, France;* [2]*FR 11.2 Organische Chemie, Universität des Saarlandes, Postfach 151150, D-66041 Saarbrücken, Germany*

*Membership of the Commission during the preparation of this report (1996–99) was as follows:
Chairman: J. R. Bolton (Canada); ***Secretary***: R. G. Weiss (USA); ***Titular Members***: J. R. Bolton (Canada); H. Bouas-Laurent (France); R. G. Weiss (USA); J. Wirz (Switzerland); ***Associate Members***: A. U. Acuña (Spain); H. Dürr (Germany); H. Masuhara (Japan); N. Serpone (Canada); ***National Representatives***: S. J. Formosinho (Portugal); P. Hrdlovic (Slovakia); B. S. Martincigh (S. Africa); U. K. Pandit (The Netherlands); B. Pandey (India); F. C. De Schryver (Belgium); S. C. Shim (Korea); V. G. Toscano (Brazil); C. H. Tung (China); C. Wentrup (Australia); I. Willner (Israel); ***Working Party for Photochromism***: H. Bouas-Laurent; R. Guglielmetti; H. G. Heller; M. Irie; J. C. Micheau; J. L. Pozzo; A. Samat.

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Organic photochromism

(IUPAC Technical Report)

Abstract: This technical report is a general introduction to organic photochromism. The definition of photochromism (PC) is given together with that of words with the ending "chromism", such as thermo-, electro-, piezo-, and tribochromism. Important concepts such as two-photon, gated, dual-mode PC and chirochromism are illustrated. The concept of fatigue (chemical degradation) and the determination of the main photochromic parameters (number of cycles, cyclability, half-life), and the spectrokinetic and mechanistic aspects are discussed. The main families of PC (organic compounds and biological receptors) are illustrated with chemical formulae, and the different types of reactions involved in the photochromic processes (pericyclic reactions, *E/Z* isomerization, group transfer, etc.) are listed. Some examples of applications to "optical power limiting" substances, photoresponsive materials, and photoswitchable biomaterials are considered.

I. INTRODUCTION

"Photochromism" is simply defined as a *light-induced reversible change of color* (a more precise definition is given in Section III); it has become a common name because many people wear photochromic spectacles that darken in the sun and recover their transparency in diffuse light. The first commercial glasses were made of glass lenses impregnated with inorganic (mainly silver) salts but in recent years, organic photochromic lenses, which are lighter and therefore more comfortable to wear despite their limited lifetime, have made an important breakthrough in the world market.

Moreover, the fact that some chemical species can undergo reversible photochemical reactions goes beyond the domain of variable optical transmission and includes a number of reversible physical phenomena such as optical memories and switches, variable electrical current, ion transport through membranes, variable wettability, etc. For this purpose, organic photochromic compounds are often incorporated in polymers, liquid crystalline materials, or other matrices.

Given the increasing use of bistable systems in materials sciences, a survey of the basic concepts and language in this developing field would be useful.

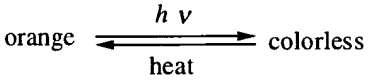
This article includes the following sections:

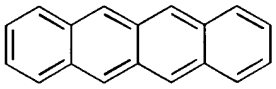
II. Brief historical survey
III. General definitions and concepts
IV. Families of organic photochromic compounds
V. Photochromic biological receptors
VI. Chemical processes involved in organic photochromism
VII. Mechanistic aspects
VIII. Applications
IX. Acronyms
X. Technical vocabulary for ophthalmic lenses
XI. Books on photochromism
XII. References
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II. BRIEF HISTORICAL SURVEY

II.1 From the first examples to the name coinage

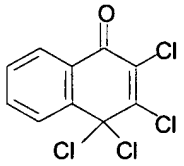
Fritzsche reported in 1867 [1] the bleaching of an orange-colored solution of tetracene in the daylight and the regeneration of the color in the dark. Later, ter Meer [2] found a change of color of the potassium salt of dinitroethane in the solid state (yellow in the dark; red in the daylight). Another early example was published by Phipson [3], who noted that a painted gate post appeared black all day and white all night (due to a zinc pigment, probably lithopone). In 1899, Markwald studied the reversible change of color of 2,3,4,4-tetrachloronaphthalen-1(4H)-one (β-TCDHN) in the solid state [4]. He believed it was a purely physical phenomenon, naming it "phototropy". Although used in that period, that term is not proper and should be avoided because it is akin to phototropism, which denotes biological phenomena (*vide infra*).





tetracene

Interest in photochromism was continuous but limited until the 1940–1960 period, which saw an increase of mechanistic and synthetic studies, particularly in the research groups of Hirshberg and Fischer in Israel. In 1950, Hirshberg [5] suggested the term "photochromism" [from the Greek words: *phos* (light) and *chroma* (color)] to describe the phenomenon. This is the name used today. However, it is not limited to colored compounds; it applies to systems absorbing from the far UV to the IR, and to very rapid or very slow reactions.



β-TCDHN

II.2 DEVELOPMENT OF THE FIELD

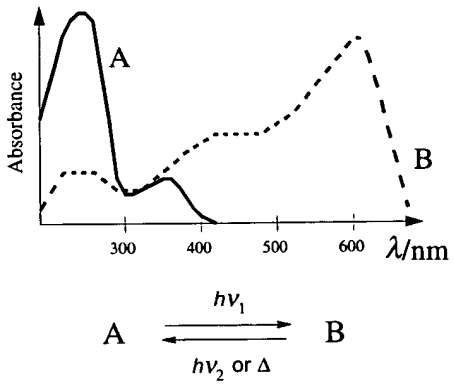
Photochromism expanded during the 1960s in parallel with the development of physical methods (IR, NMR, X-ray, UV, time-resolved and flash spectroscopy) and organic synthesis. Photochromic glasses became available at that period and further stimulated research. Applications, such as the photochromic micro image (PCMI) process, which showed the possibility of reducing the 1245 pages of a Bible to about 6 cm^2, attracted considerable interest. An important book was published in 1971 [6]. However, it appeared that the photodegradation of the known families of organic photochromes limited their potential for applications [7].

A revival of activity started in the 1980s, essentially because of the development of fatigue-resistant *spirooxazine* and *chromene* derivatives. They triggered the fabrication and commercial application of photochromic ophthalmic lenses. Since then, other commercial systems have been developed, and new photochromic systems have been discovered and explored. In parallel, several books have been printed (*vide infra*); a flow of articles in scientific journals has appeared and International Symposia on Photochromism (ISOP) have been organized.

III. GENERAL DEFINITIONS AND CONCEPTS

III.1 Definition of photochromism

"Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different[a] absorption spectra".



The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (*Photochromism of type T*) or photochemically (*Photochromism of type P*).

The most prevalent organic photochromic systems involve *unimolecular* reactions: the most common photochromic molecules have a colorless or pale yellow form A and a colored form B (e.g., red or blue). This phenomenon is referred to as *positive photochromism*. Other systems are *bimolecular*, such as those involving photocycloaddition reactions. When $\lambda_{max}(A) > \lambda_{max}(B)$, *photochromism* is *negative* or *inverse*.

The unimolecular processes are encountered, for example, with *spiropyrans*, a family of molecules that has been studied extensively. Solid photochromic spiropyrans or solutions (in ethanol, toluene, ether, ketones, esters, etc.) are colorless or weakly colored. Upon UV irradiation, they become colored. The colored solutions fade *thermally* to their original state; in many cases, they can also be decolorized (*bleached*) by visible light. A few spiropyrans display negative photochromism. They are colored in the dark and *bleached* by UV light. Many spiropyrans are also *thermochromic* (see definition below), and spectra of the colored forms are identical to those produced photochemically.

III.2 One-photon and two-photon systems

In general, the photochromic processes involve a one-photon mechanism. B is formed from the singlet ($^1A^*$) or triplet ($^3A^*$) excited states or both. B, the photoproduct, may also be formed from an upper excited state populated by absorption of two photons.

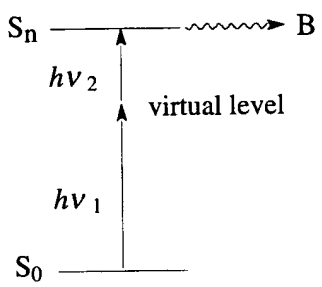
Two-photon photochromism

The transition probability to populate the final state (hence to obtain the photoproduct) depends on the product of the photon irradiances $E_{p(1)}$ and $E_{p(2)}$ of the two exciting beams.

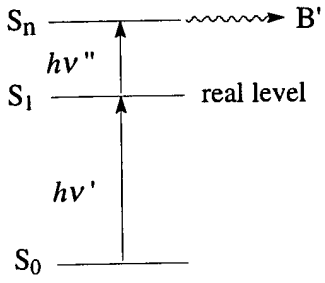
It is, therefore, advantageous to utilize lasers emitting high photon irradiance, such as those generating picosecond or subpicosecond pulses. Two absorption processes may be distinguished:

a) simultaneous absorption of two photons via a virtual level.
b) stepwise (or sequential) two-photon absorption where the second photon absorption takes place from a real level.

[a]The difference in spectrometric (optical) properties is accompanied by a difference of other physical properties.



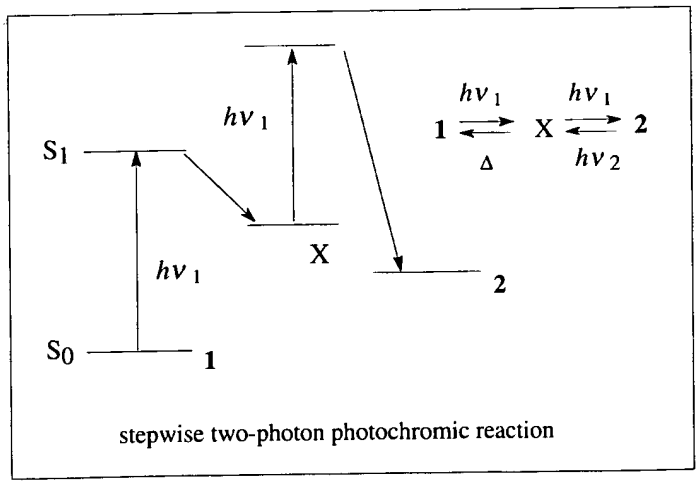
simultaneous two-photon absorption leading to product B



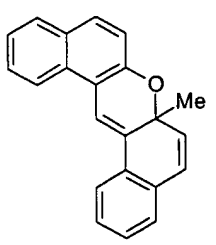
stepwise two-photon absorption leading to product B'

The simultaneous process (a) has been successfully used for exciting photochromic molecules at specific positions inside a volume for 3D memory systems (writing process). A two-photon absorption process was also used to excite the written molecules that emit fluorescence (reading process) [8,9].

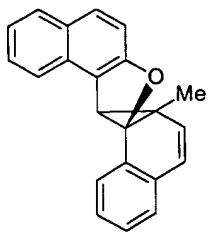
The excitation process can also proceed through a metastable intermediate (process b) as with the dinaphthopyran derivative (**1**). It was found to isomerize to the bicyclohexene derivative (**2**) via an intermediate X (not isolated). The authors used two 405-nm photons and observed that the quantum yield $\Phi_{1->2}$ is proportional to the square of the photon irradiance. The reverse reaction **2** → **1** was found to proceed at 334 nm [10].



stepwise two-photon photochromic reaction



1



2

III.3 Photochromic compounds

Photochromic compounds are chemical species having photochromic properties. The following terms, sometimes used as synonyms, should be avoided: "Photochromics" is colloquial; "photochromes" are proofs in color photography; "photochromy" is a former technique of color photography.

III.4 Phototropism

Phototropism, observed in plants, refers to a light-induced growth response directed toward or away from the light.

III.5 Chromism

Chromism, as a suffix, means "reversible change of color" and, by extension, a reversible change of other physical properties. The prefix indicates the phenomenon inducing the change [e.g., *chromism induced by light* (or electromagnetic radiation) is photochromism]. The following are related to photochromism.

III.6 Heliochromism

Heliochromism was coined by Heller [11]. Heliochromic compounds have a high efficiency for coloring with near UV radiation and a low efficiency for bleaching with visible light, but a moderate efficiency for thermal fading at ambient temperatures. They are activated by unfiltered sunlight and deactivated under diffuse daylight conditions. Therefore, they are suitable for *sun lens applications*.

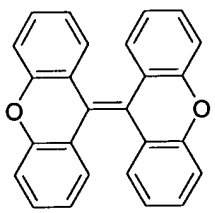
III.7 Electrochromism

Electrochromism is the reversible change of absorption spectra between two forms, A and B, resulting from electrochemical (oxidation/reduction) reactions [12].

III.8 Thermochromism

Thermochromism is a thermally induced reversible color change. A large variety of substrates, such as organic, inorganic, organometallic, and macromolecular systems (e.g., polythiophenes) or supramolecular systems (such as liquid crystals) exhibit this phenomenon. Spiroheterocycles (spiropyrans, spirooxazines), Schiff bases, and bianthrones are well-known *thermochromic organic* compounds. When the thermochromism of molecular systems results from association with another chemical species such as a metal ion or proton or from modification of the medium by a thermal effect, the phenomenon is called "thermosolvatochromism" [13].

9,9'-Bixanthenylidene, a typical thermochromic molecule, is *colorless* at liquid nitrogen temperature, *yellow-green* at room temperature and *dark-blue* when melted or heated in boiling mesitylene [14].



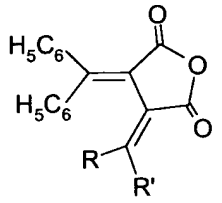
9,9'-Bixanthenylidene

III.9 Piezochromism

Piezochromism is the phenomenon when crystals undergo a major change of color *due to mechanical grinding*. The induced color *reverts* to the original color when the fractured crystals are kept in the dark or dissolved in an organic solvent. The grinding generates a metastable form (see tribochromism). An example of a piezochromic organic compound is diphenylflavylene [15].

III.10 Tribochromism

Tribochromism is the phenomenon when crystals undergo a major change of color *during mechanical grinding* (as is the case of piezochromism), but the induced color change *does not revert* to the original color when the fractured crystals are kept in the dark or dissolved in an organic solvent. The crystals, prior to fracture, are in a metastable state [16].



R, R' = cycloalkylidene
R, R' = alkyl or cycloalkyl

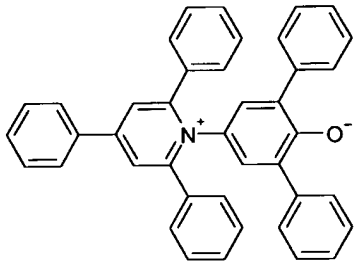
General formula of some tribochromic compounds

III.11 Solvatochromism

Solvatochromism is the reversible variation of the electronic spectroscopic properties (absorption, emission) of a chemical species, induced by solvents [17,18].

III.12 Halosolvatochromism

Halosolvatochromism is a color change upon increasing ionic strength of the medium without a chemical change of the chromophore.



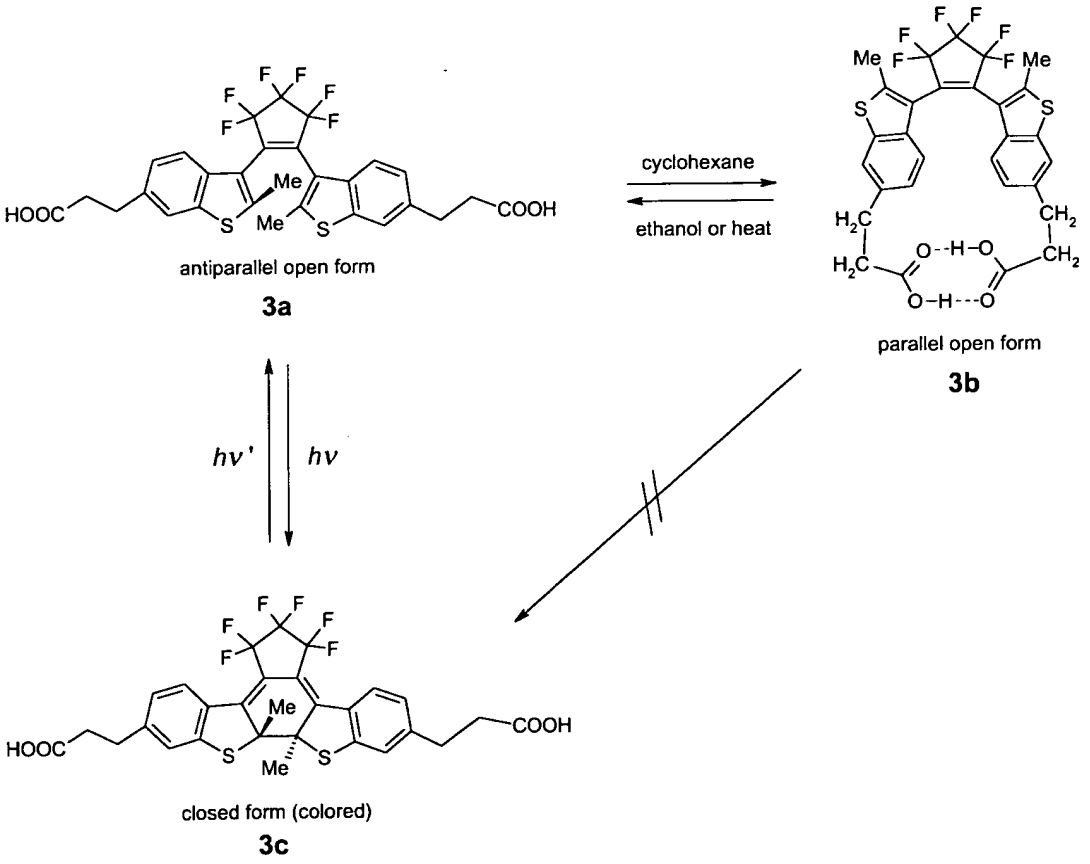
2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide

Examples are solutions of the betaine dye shown above. It undergoes a very large solvatochromic effect, which is the basis of an empirical parameter of solvent polarity, the $E_T(30)$ scale. Furthermore, the addition of salts such as KI, $Ca(SCN)_2$, or $Mg(ClO_4)_2$ to solutions of the betaine dye in acetonitrile also induces a hypsochromic shift of the electronic absorption spectrum that increases with the charge density of the cations. The combination of both properties is termed "halosolvatochromism" [19].

III.13 Gated photochromism

Gated photochromism is a special type of photochromism in which one or both forms of the photochromic system are transformed (chemically or electrochemically) reversibly into a nonphotochromic form. The photochromic process is controlled like the flow through a gate. The opening or closing of the gate may depend on external stimuli such as protonation, oxido-reduction, solvation, and temperature. Gated photochromism is illustrated with the following example [20].

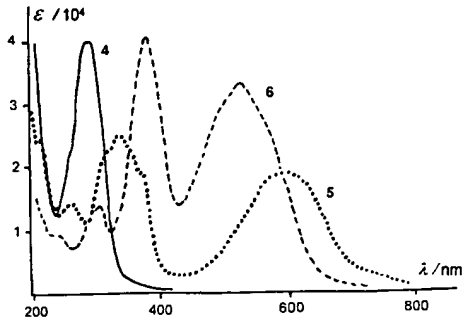
The conrotatory photocyclization of diarylethene **3** proceeds only from the antiparallel form (**3a**) in ethanol. The cyclization is completely inhibited in cyclohexane or decalin, where the parallel form (**3b**) is *maintained* by H-bond formation. Heating at 100 °C (or adding EtOH) disrupts the intramolecular H-bonds and allows the photochromic reaction to occur between **3a** and **3c**.



adapted from [20] with permission; copyright 1992 American Chemical Society

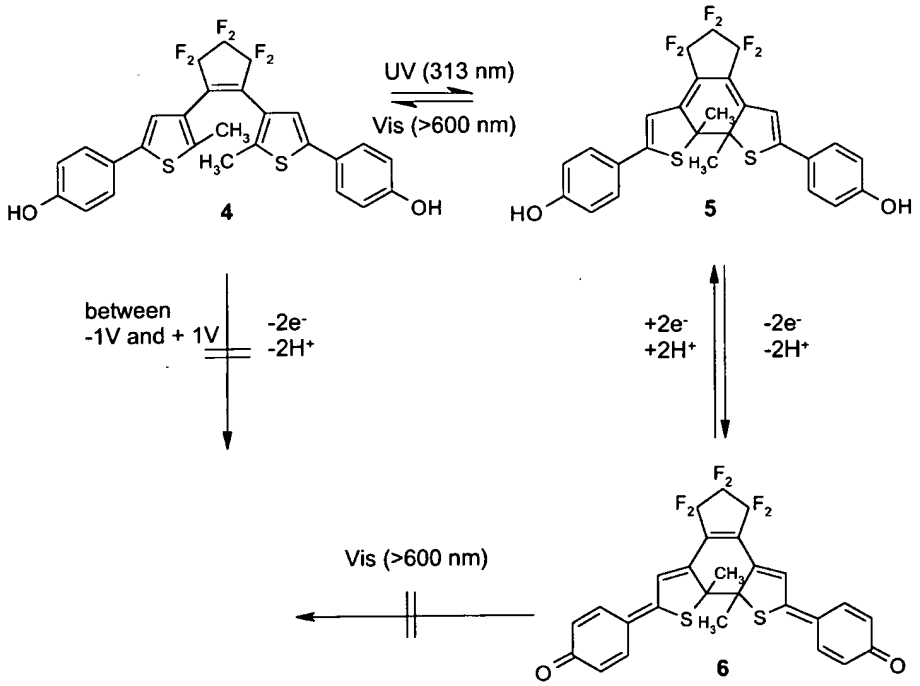
III.14 Dual-mode photochromism

Dual-mode photochromism occurs in complex systems triggered alternatively by two different external stimuli, such as light and an electric current. In such a case, photochromism and electrochromism are mutually regulated. The following substrates have been proposed as suitable for a dual-mode optoelectrical molecular switching device [21]. The device may be reversibly converted among states **4**, **5**, and **6**, which are all thermally stable and exhibit very distinct absorption spectra (shown below).



adapted from [21], by permission of the Royal Society of Chemistry

Compound **4** may be reversibly transformed to **5** photochemically, **4** being electrically inert and **5** being active and reversibly oxidized to **6** within the −1 to +1V range.

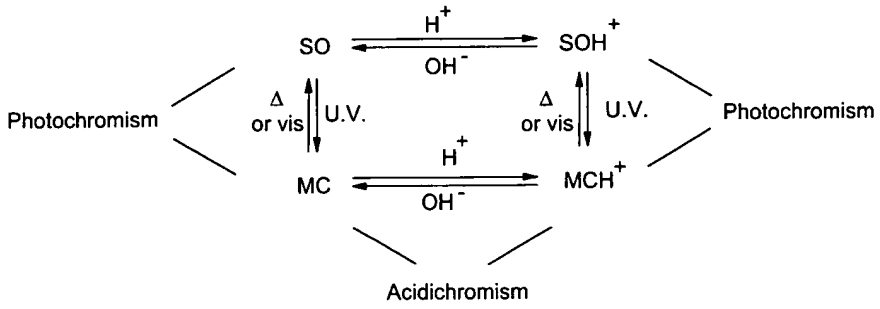


Further, the system can be electrochemically interconverted between the reduced form **5** (which is photochromic) and the quinoid species **6**, which is photochemically stable. Therefore, after *writing* with UV light, the information may be safeguarded by an electrochemical process (**5** → **6**) and *readout* at *ca* 600 nm; after electrochemical reduction (**6** → **5**), the information may be *erased* with visible light.

A dual-mode photoswitching of luminescence has been described [22]. (See also chirochromism).

III.15 Acidichromism

In acidichromism, the protonated form and the conjugate base of some compounds may have distinctly different absorption spectra. This phenomenon is well known for phenols and aromatic amines. *It can occur in addition to photochromism*, e.g., for spirooxazines (SO) which generate merocyanines (MC) [23] as illustrated in the following scheme:



In some cases, it is possible to take advantage of acidichromism to develop nondestructive readout systems in which one of the forms can be used for readout and the others for writing and erasing [24].

III.16 Ionochromism

Ionochromism is a reversible change of color by addition of salts. It can occur in addition to photochromism and may trigger a modulation of conductivity. (See scheme for acidichromism and replace H^+ by M^+).

III.17 Halochromism

Halochromism, a term introduced by von Baeyer [25], denotes the trivial color change of a dye on addition of acids or bases. It is caused by the formation of a new chromophore, as in acid-base indicators (see acidichromism).

$$\underset{\textit{colorless}}{\text{Example : } \Phi_3C\text{–Cl} + AlCl_3} \rightleftarrows \underset{\textit{yellow}}{\Phi_3C^+ + AlCl_4^-}$$

III.18 Chirochromism

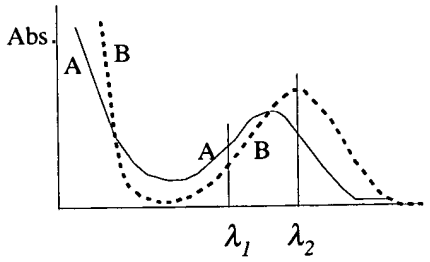
III.18.1 Chirochromism

Generally, chirochromism is a reversible change of rotation of the plane of polarized light between two chiral diastereomers of a photochromic system (*vide infra*). It should be noted that the interconversion of two enantiomers of a photochromic compound which have, by definition, identical absorption spectra in *nonchiral media*, does not pertain to photochromism; however, these enantiomers might exhibit different absorption spectra in *chiral media*, especially in solid matrices.

III.18.2 Diastereoselective photochromism (diastereophotochromism)

Diastereoselective photochromism (diastereophotochromism) is a photoinduced reversible change of absorption spectra between two diastereomers A and B. The diastereomeric excess (E_{dia}) at the photostationary state (pss), from irradiation of a mixture of A and B at the wavelength λ with nonpolarized light, depends on the molar absorption coefficients (ε) and the interconversion quantum yields, $\Phi_{AB}(A \rightarrow B)$ and $\Phi_{BA}(B \rightarrow A)$, according to the following equation [26]:

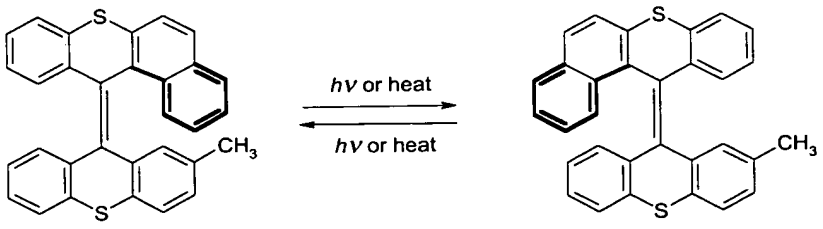
$$[E_{dia}]_{pss} = \frac{[A]-[B]}{[A]+[B]} = \frac{(\varepsilon_B \Phi_{BA} - \varepsilon_A \Phi_{AB})\lambda}{(\varepsilon_B \Phi_{BA} + \varepsilon_A \Phi_{AB})\lambda}$$



The mixture (A,B) will result in an enrichment of B at λ_1 and of A at λ_2.

If A and B contain chiral subunits, their interconversion will result in different effects on plane polarized light (which can be measured by circular dichroism); this reversible interconversion is referred to as "chirochromism".

Enantiomerically pure, sterically overcrowded heterocycles, **7** (*cis*) and **8** (*trans*), exhibit a stereospecific photochemical isomerization of **7** to **8** and **8** to **7** (diastereophotochromism); the two diastereoisomers have been shown to be thermally stable, and no isomerization was detected at ambient temperature in the dark. The reaction is also thermally controlled (*diastereothermochromism*); the isomerization is accompanied by a simultaneous reversal of helicity and can be followed by circular dichroism. Such a system can be a *chiroptical molecular switch* [27].



7 (*cis*) **8** (*trans*)

Related chiral photochromic molecules [28] were shown to display different fluorescence emission spectra which are regulated by reversible protonation. It is another case of *gated photochromism* (see definition).

III.19 Colorability

Colorability is the ability of a colorless or a slightly colored (pale yellow) photochromic material to develop coloration. In dilute solutions, the initial absorbance "$A_0(\lambda)$" immediately after photolysis is proportional (proportionality constant k includes the incident photon flux) to Φ_{col} (coloration quantum yield), ε_B (molar absorption coefficient of the colored form), and c_A (concentration of colorless form) at a given irradiation wavelength [29].

$$A_0(\lambda) = k\, \Phi_{col}\, \varepsilon_B\, c_A$$

III.20 Fatigue

Photochromism is a nondestructive process, but side reactions can occur. The loss of performance over time, due to chemical degradation of a material, is termed "fatigue". Usually, the major cause of damage to photochromic substances is oxidation [30].

The following are examples of particularly fatigue-resistant substances:

a) Single crystals of methyl-substituted *dithienylperfluorocyclopentenes* are stable at 100 °C and can be cycled more than 10^5 times without loss of their shape. Because of physical damage due to surface reconstruction during photoisomerization, transmittance of the single crystals started to decrease after 10^4 cycles [31].

b) *Bacteriorhodopsin* from the purple membrane of "Halobacterium halobium" is reported to undergo more than 10^5 photochemical cycles without damage [32].

III.21 Number of cycles

The number of cycles that a system can undergo under well-defined conditions (solution, matrix, concentration, temperature) is an important experimental parameter. In a *cycle*, a system A is transformed (photochemically) into system B which returns to A (thermally or photochemically); the terms "switch on" and "switch off" are used.

Ideally, the yields of the two reactions are quantitative, but byproducts are actually formed. If the degree of degradation in a cycle is x, the nondegraded fraction y after n cycles will be:

$$y = (1-x)^n$$

For very small x and very large n, this expression can be approximated as:

$$y \approx 1 - nx$$

Thus, for $x = 0.001$ (yield = 99.9%), after 10^3 cycles, 63% of A will be lost, and after 10^4 cycles virtually no A will be present.

III.22 Cyclability (Z_{50})

Z_{50} is the number of cycles required to reduce the initial absorbance at a specific wavelength by 50% [33].

III.23 Half-life ($T_{1/2}$)

$T_{1/2}$ is the time necessary for thermal bleaching to half of the absorbance of the colored form at a specific wavelength during one cycle. (See cyclability and thermal fade rate.)

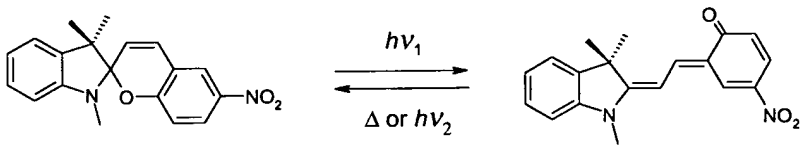
III.24 Readout number

For application to ROM (read only memory) devices, a useful parameter is the number of readings under continuous irradiation. Assuming the reading time to be ≈10 μs, there can be up to 8×10^9 readings per day.

IV. FAMILIES OF ORGANIC PHOTOCHROMIC COMPOUNDS

In all cases, $h\nu_2 < h\nu_1$.

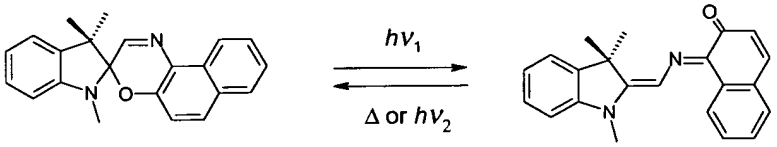
IV.1 Spiropyrans



Closed Form

Open Form (Merocyanine)
(Quinonic form)

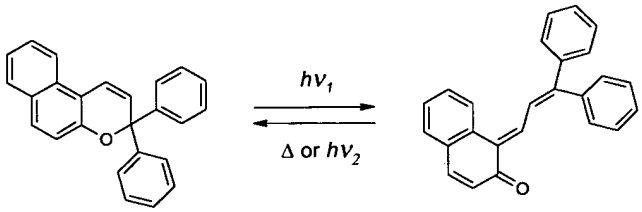
IV.2 Spirooxazines



Closed Form

Open Form (Merocyanine)
(Quinonic form)

V.3 Chromenes

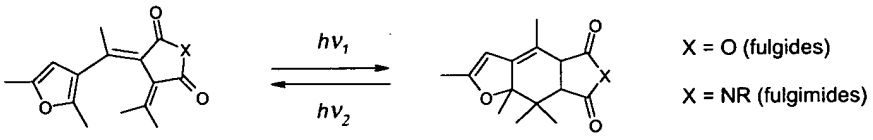


Closed Form

Open Form

IV.4 Fulgides and fulgimides

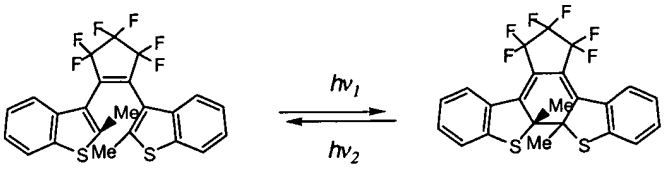
The name "fulgides" (from the Latin *fulgere*, to glisten) was given by their first investigator, Stobbe, because they were isolated as fine glittering crystals. Their photochromic properties have been studied extensively by Heller [34].



Open Form

Closed Form

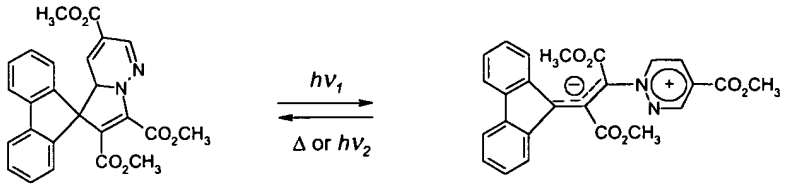
IV.5 Diarylethenes and related compounds



Open Form

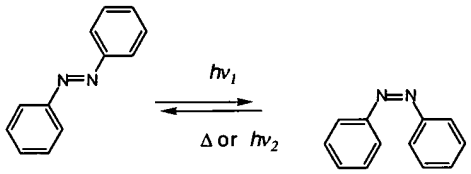
Closed Form

IV.6 Spirodihydroindolizines



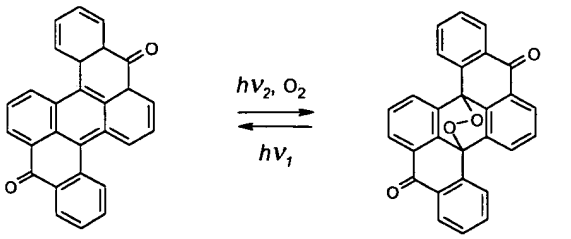
Closed Form Open Form

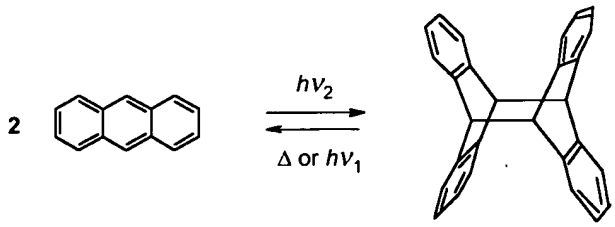
IV.7 Azo compounds



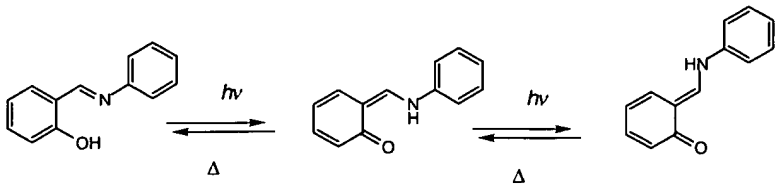
trans (anti) *cis (syn)*

IV.8 Polycyclic aromatic compounds



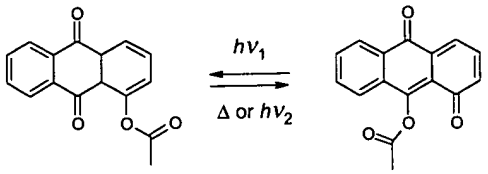


IV.9 Anils and related compounds (hydrogen transfer)

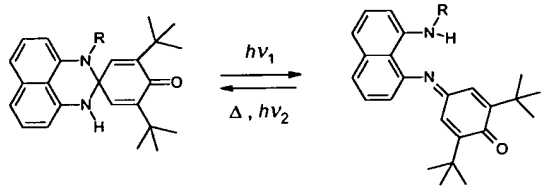


NB: Aldehydes react with primary amines to form imines (Schiff bases). When the amine is aniline, the imine is known as an "anil".

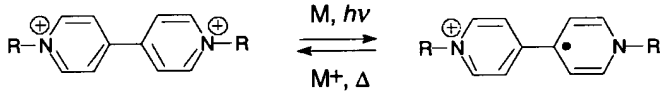
IV.10 Polycyclic quinones (periaryloxyquinones)



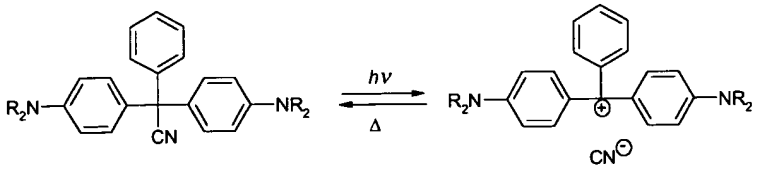
IV.11.Perimidinespirocyclohexadienones



IV.12 Viologens



IV.13 Triarylmethanes

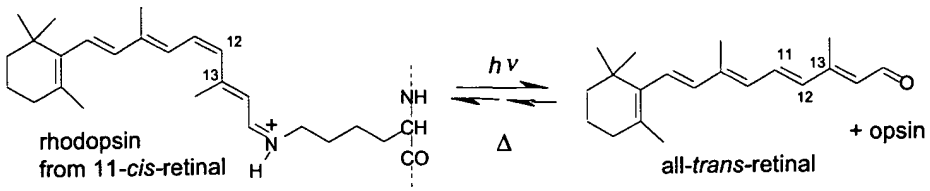


V. PHOTOCHROMIC BIOLOGICAL RECEPTORS

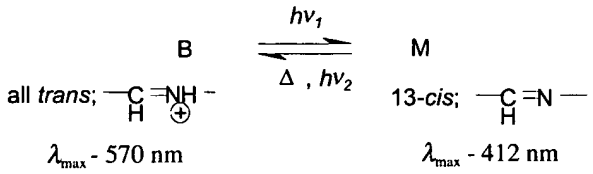
Many biological systems are photochromic, but few remain so when isolated from the living cell of which they are part [35].

V.1 Retinal proteins

Rhodopsin: the chromophore, retinal, is bound to a protein via a lysine through a protonated Schiff base. The complex photochromic cycle is outlined below:

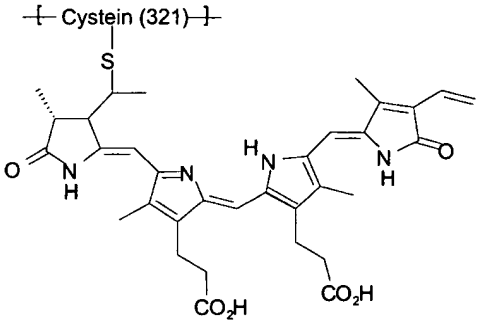


Bacteriorhodopsin (BR): the retinal is also bound to a lysine fragment of a protein present in the purple membrane (PM) of halobacterium halobium; a simplified model of the BR photocycle involves forms B and M as follows:

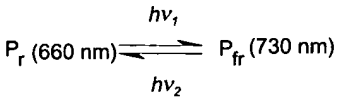


V.2 Phytochrome (P)

Phytochrome (P) controls the photomorphogenesis of plants.



structure of the Pr form (660 nm)



r= red, absorbing in the red

fr= far-red, absorbing in the far-red

VI. CHEMICAL PROCESSES INVOLVED IN ORGANIC PHOTOCHROMISM

VI.1 Pericyclic reactions

Electrocyclizations, whether concerted or not concerted, are 6π 6 atom processes for spiropyrans, spirooxazines, chromenes, hexa-1,3,5-triene, diheteroarylethenes, and cyclohexa-1,3-diene systems, and 6π 5 atom processes for spirodihydroindolizines and other pyrazoline based systems.

Cycloadditions are found in (2+2) cycloadditions based on valence isomerizations or in molecules with multiple bonds incorporated in or linked to aromatic systems. (4+4) Cycloadditions are found mainly in polycyclic aromatic hydrocarbons. (4+2) Cycloadditions are found, for example, in additions of singlet oxygen to aromatic compounds.

VI.2 *Cis-trans* (*E/Z*) isomerizations

Cis-trans (*E/Z*) isomerizations occur in stilbenes, azo compounds, azines, thioindigoids, etc., as well as some photochromic biological receptors that are part of living systems.

VI.3 Intramolecular hydrogen transfer

Intramolecular hydrogen transfer is found in anils, benzylpyridines, aci-nitro and related compounds, salicylates, triazoles, oxazoles, metal dithizonates, and perimidinespirohexadienones.

VI.4 Intramolecular group transfers

Intramolecular group transfers operate in polycyclic quinones (periaryloxyparaquinones).

VI.5 Dissociation processes

Heterolytic bond cleavages occur in triarylmethanes and related systems. Homolytic bond cleavages are found in triarylimidazole dimers, tetrachloronaphthalenes, perchlorotoluene, nitrosodimers, hydrazines, etc.

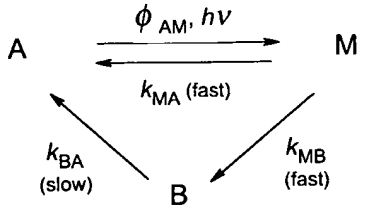
VI.6 Electron transfers (oxido-reduction)

Electron transfers (oxido-reduction) are photoinduced in viologens and related systems. The same compounds can also undergo electrochromism.

VII. MECHANISTIC ASPECTS

VII.1 Kinetics of photochromic compounds

The determination of the photochromic parameters, such as the number, nature, and kinetic and spectral properties of the transient species formed under irradiation, is not a trivial task because the photoproducts are too labile to be isolated in many cases. As an illustration, the kinetic behavior of the unimolecular systems is considered (e.g., spiropyrans, spiroxazines, dihydroindolizines, which are of major importance for applications to ophthalmic lenses). It can be accommodated in the following scheme:



(1)

It involves **A**, the noncolored "closed" form (see IV.1,2,6), **M**, a short-lived transient species (a singlet and/or triplet excited state or a very labile photoisomer), and **B**, the long-lived but not isolable colored "open" form.

The analysis can be performed using either pulsed or continuous irradiation methods.

a) Pulsed irradiation: Immediately after a light pulse, only **M** has accumulated.
b) Continuous irradiation: Using a low-power photon flux, a product such as **B** (often a photoisomer) can accumulate over time scales of 10^{-2}–10^{+6} s.

In order to estimate some relevant parameters related to photoisomer **B** (quantum yields as well as UV/visible spectra), specially designed kinetic experiments must be carried out. Under continuous monochromatic irradiation, a photochromic system can be considered to be at nonequilibrium and open. The evolution of the concentrations of the reacting species (starting compounds, photoisomers, and degradation products) can be described by an appropriate set of differential equations. The only simplifying hypothesis that is used for their establishment is that the well-stirred mixture obeys Beer's law. UV/visible multiwavelength analysis of absorbance vs. time curves recorded under continuous monochromatic irradiation provides information about the evolution of the corresponding concentrations [36]. Simulated curves from numerical integration of the differential equations generated from the kinetic scheme are compared with the experimental curves using curve-fitting procedures.

An example of a typical kinetic analysis of a unimolecular photochromic system under continuous monochromatic irradiation and following the above kinetic scheme (1) is given in Fig. 1.

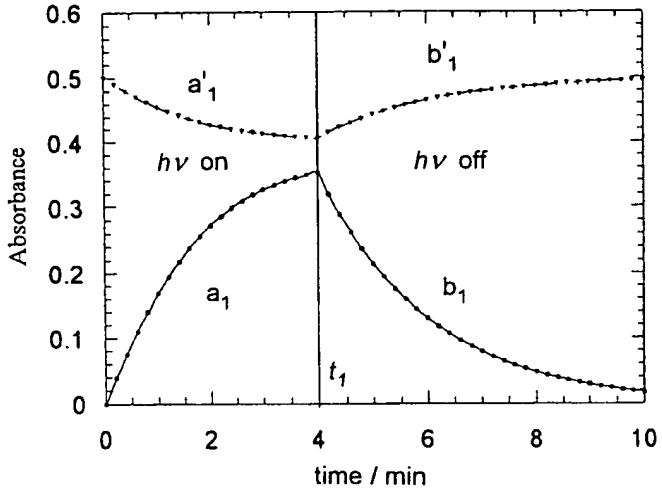


Fig. 1 Evolution of the absorbance at two wavelengths of a unimolecular photochromic system under continuous irradiation. Curves a_1 and b_1 are monitored at the λ_{max} of the open form, while a'_1 and b'_1 are at the irradiation wavelength (λ_{irr}). UV irradiation has been stopped at time t_1. The thermal rate constant k_{BA} is extracted from the relaxation processes (b_1 and b'_1 from $t_1 \rightarrow \infty$) in the dark, while Φ_{AB} and ε_B are extracted from the kinetic curves under irradiation (a_1 and a'_1 corresponding to the irradiation periods 0-t_1). Knowledge of the evolution of the absorbance at the irradiation wavelength (λ_{irr}) allows the fraction of incident photon flux that is really absorbed by the photochromic starting compound **A** to be calculated.

More complex situations that include photobleaching and photodegradation or the presence of several interconverting photoisomers (as in the case of chromenes) can also be treated by similar methods [37].

VII.2 Photochromic behavior and spectrokinetic properties

The coloration efficiency (see "colorability") is given by the absorbance $A_0(\lambda)$ at the maximum wavelength of the colored form immediately after a pulse of radiation ($t = 0$). This parameter obtained under standard conditions (concentration of the closed form ca. 2.5×10^{-5} M, in toluene solution, at 25 °C) for a series of photochromic colorless compounds such as spiropyrans, spirooxazines, chromenes, etc. (together with the maximum wavelength of their visible absorption spectra), is an indicator of their relative photochromic behavior. Other important data are the first-order thermal decay rate constants (k_Δ) and the time ($t^*_{(A_{0/2})}$), necessary to obtain half of the initial colorability after continuous irradiation (test of fatigue). Table 1 reports values obtained for some examples of typical photochromic compounds in toluene solution [38]. It is useful for selecting the suitable derivatives for a particular purpose, but the photochromic properties may be different in polymers and vary according to the nature and the oxygen content of the matrix.

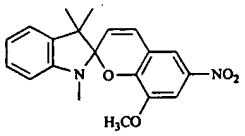
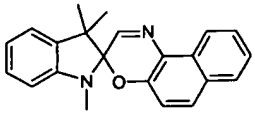
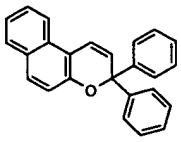
VII.3 Photochromic parameters measurements

A computer-controlled apparatus [30,38] has been constructed to determine the main parameters describing some photochromic properties such as colorability $A_0(\lambda)$, thermal bleaching rate constant (k_Δ), and the time necessary to reach half of the initial absorbance ($t^*_{(A_{0/2})}$, reflecting fatigue resistance).

The apparatus can be operated in three modes:

a) Pulsed irradiation: Sequences of several excitation pulses are followed by a detection pulse; n_R is the number of pulses necessary to reach the $A_{0/2}$, the half value of the colorability $A_0(\lambda)$.
b) Cyclic mimicking a daylight exposure: Sequences of successive bright continuous irradiation and dark periods are carried out until the $A_{0/2}$ value is obtained.
c) Continuous: Sequences are the same as in the cyclic mode but the dark period is reduced to 1 min to stabilize the photomultiplier tube.

Table 1. Photochromic parameters in diluted toluene solutions.

Compound (2.5×10^{-5}M) in toluene	Colored Form λ_{max}/nm	$A_0(\lambda)$ t=0	k_Δ /s^{-1}	$t^*_{(A_{0/2})}$
 6-nitro-8-methoxy BIPS	615	4.6	0.02	7.5 min
 1,3,3-trimethylspiro[indoline-naphthoxazine]	594	1.08	0.54	8.5 h
 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran	432	0.84	0.09	7.5 h

VIII. APPLICATIONS

VIII.1 General applications

General applications of photochromism can be divided into two categories:

a) those directly related to the change in absorption or emission spectra such as variable transmission optical materials, optical information storage, cosmetics, authentication systems, and flow-field visualization
b) those related to other physical or chemical property changes such as refractive index, dielectric constant, electric conductivity, phase transitions, solubility, viscosity, and surface wettability

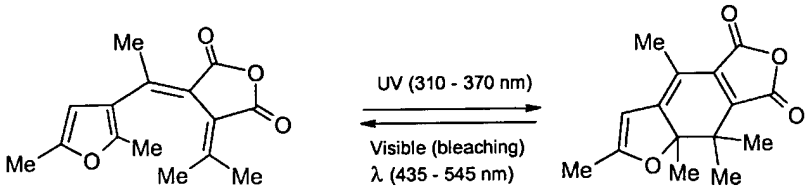
The most famous application is sunglassses; some other potential applications are described below.

VIII.2 Actinometry

"An actinometer is a chemical system or a physical device which determines the number of photons in a beam integrally or by unit time..." as defined in the "Glossary of Terms Used in Photochemistry" [39].

Chemical actinometry in solution has the advantage over physical actinometry in that the former can be used under conditions similar to those of the photoreaction to be studied [40]. In addition, photochromic actinometers can be used repeatedly, thus obviating the need for a fresh sample for each measurement. Some thermally stable photochromic compounds, such as the following, fulfil this requirement.

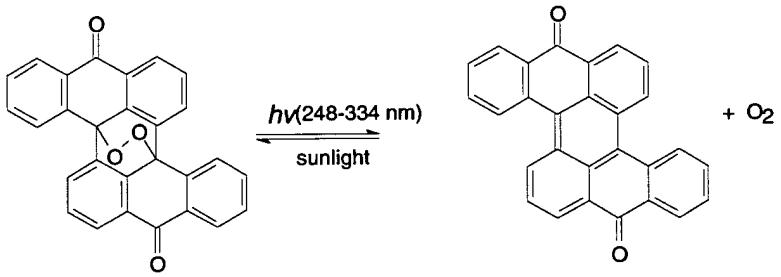
AberchromeTM540 is well suited for chemical actinometry within the range 310–370 nm (coloring reaction) and 435–545 nm (decoloration) domains [41a]. It should be noted that it is useful at 365 nm where several other actinometers are inappropriate.



The quantum yield for coloring is temperature-independent (5–55 °C). It can be used repeatedly when a 5×10^{-3} mol dm^{-3} toluene solution is employed. A drop in quantum yield is found on repeated use at lower concentrations [41b–e].

Azobenzene $>6 \times 10^{-4}$ mol dm^{-3} in methanol can be used in the 254–334 nm range [42a,b]. The absorption spectra of the *trans* and *cis* isomers differ sufficiently to produce significant changes in absorbance during the photoisomerization.

Heterocoerdianthrone endoperoxide (HECDPO) is a suitable actinometer in the 248–334 nm region. It is formed from an air saturated solution of heterocoerdianthrone (HECD) in methylene chloride that has been in sunlight with a 420–480 nm band pass filter and stored in the dark [43]. Between 253 and 302 nm, the reaction efficiency does not depend on irradiation wavelength.

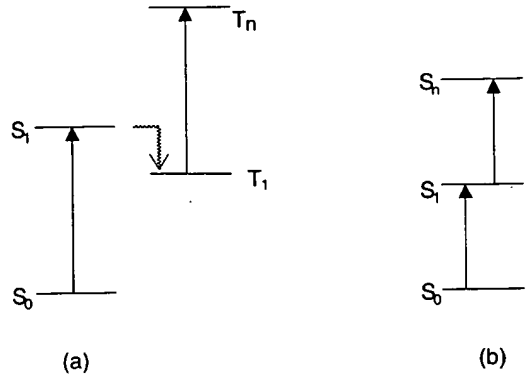


HECDPO (colorless) HECD (red)

VIII.3 Optical power-limiting substances

Optical power-limiting substances are used to protect the human eye or optical sensors from the damaging effects of intense flashes of light. An *ideal limiter* becomes suddenly opaque during exposure to a laser burst and immediately transparent again at the end of the pulse. Compounds that are potential optical limiters are *fullerenes, indanthrones, porphyrins, mixed metal clusters*, and *phthalocyanines* (especially chloroindium phthalocyanine) [44,45].

The phenomenon is caused by the promotion of a very large fraction of the molecule from the ground state to an excited state, which absorbs photons more strongly than the ground state.



This excited state may be the T_1 (a) or the S_1 state (b). Under these conditions,

$$\int \varepsilon(\nu)_{T_1 \rightarrow T_n} d\nu >> \int \varepsilon(\nu)_{S_0 \rightarrow S_1} d\nu \qquad \text{(a)}$$

or

$$\int \varepsilon(\nu)_{S_1 \rightarrow S_n} d\nu >> \int \varepsilon(\nu)_{S_0 \rightarrow S_1} d\nu \qquad \text{(b).}$$

VIII.4 Photoresponsive materials

Reversible photoinduced changes of physical and chemical properties can be transferred to the micro-environment by a photochromic molecule incorporated in the system (Fig. 2).

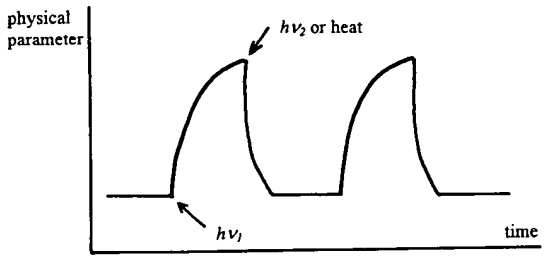


Fig. 2 Photoinduced cyclic variation of a physical property in a photoresponsive system.

Some examples are given below:

- Photomechanical effects: Reversible photomechanical deformation could be observed using Brewster angle optical microscopy with monolayers of polyvinyl alcohol bearing an azobenzene side chain, "PVA-AzB" derivatives, on water surface [46].
- Chiroptical molecular switches: Photoisomerization of photochromic units (azobenzenes, spiropyrans, etc.) in poly(α-amino acid)s is able to trigger a random coil to α-helix transition. This primary photochemical event occurring in the side chains is amplified and transduced by the structural variations of the macromolecular main chains. The latter are accompanied by large and reversible variations of optical activity [47]. Because of their reversibility, these systems can act as "chiroptical molecular switches" (see also [27]).

- Sol-gel transition temperature: 1% Aqueous solutions of poly(N-isopropylacrylamide) can form thermoreversible gels [48]. Pendant azobenzene groups (2.7 mol %) have been shown to change reversibly the gelation temperature. At 750 nm, the solution is transparent, whereas the gel is opaque as shown in the graph below (Fig. 3).

The *cis* form of azobenzene maintains a high percent transmittance between 20 °C and 26 °C ($t_{sol\text{-}gel} \approx 30$ °C), whereas the *trans* isomer induces a sol-gel transition temperature around 20 °C. These transition temperatures are controlled by light (λ_1 or λ_2) which triggers *cis-trans* isomerization, so that the transmittance can be tuned from 80% to 0% (or 0% to 80%) by irradiation in the 20–26 °C temperature range [48].

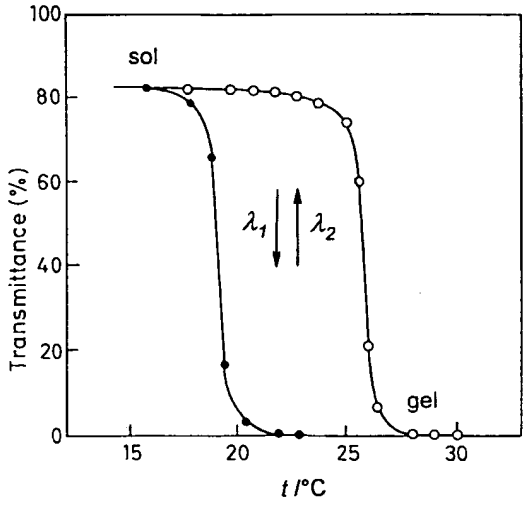


Fig. 3 Transmittance variation at 750 nm of the photochromic solution (see text) vs. temperature; ● in the dark; ○ upon photoirradiation. Irradiation at 350 nm < λ_2 < 410 nm solubilizes the polymer, and the solution becomes transparent; visible irradiation at λ_1 > 410 nm decreases the solubility, and the polymer leads to phase separation. (Adapted from [48] with permission; copyright 1990 Springer Verlag.)

VIII.5 Photoswitchable biomaterials

The combination of biomaterials and photochromic compounds is the basis for the design of optobioelectronic devices. The following example, describing a *photoreversible immunosensor electrode* (see Fig. 4), illustrates the contribution of photochromism to the development of biomaterials science [49].

The antigen (Atg) functionalized gold electrode, modified by a self-assembled monolayer (**a**), yields an amperometric signal in the presence of a redox probe (R^+/R). Association of the antibody (Ab) to the monolayer (**b**) insulates the electrode towards the solubilized redox probe resulting in the absence of an electrical signal. Owing to the tight "Atg-Ab" association, such electrodes are limited to a single analysis. But the antigen can be chemically modified by a photochromic component (A) which does not impede the amperometric sensing of the antibody. The antigen monolayer will be perturbed by photoisomerization of A into B and will release the antibody (**c**). The active Atg monolayer (**a**) is regenerated by the reverse photoisomerization B → A. Further analyses are thus possible.

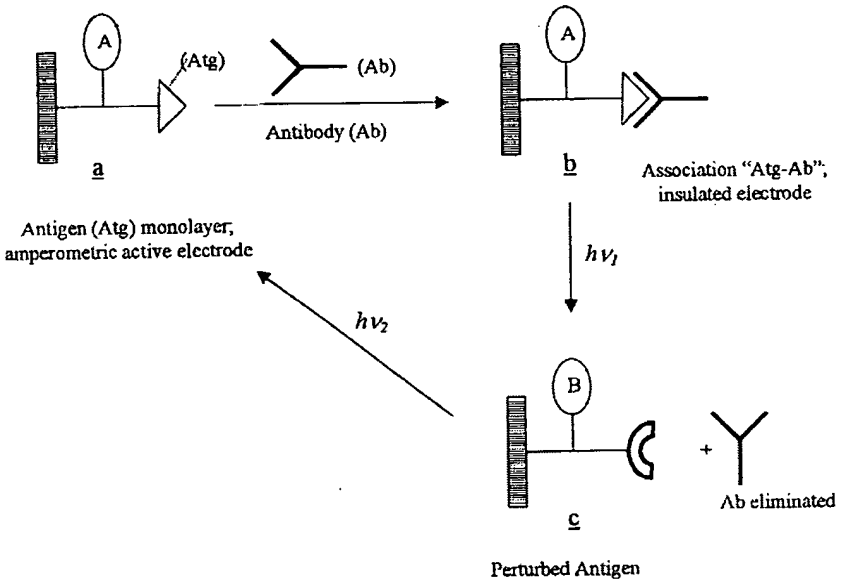
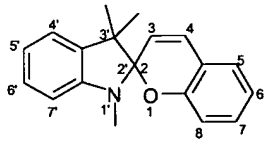


Fig. 4 Schematic assembly of a photoreversible immunosensor electrode. Reproduced from [49] with permission; copyright 1997 American Chemical Society.

IX. ACRONYMS

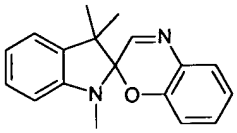
ARPO aromatic endoperoxide

BIPS "Benzo Indolino Pyrano Spiran"



BIPS are derivatives of
1', 3',3' – trimethylspiro (2*H*-1-benzopyran-2,2'-indoline)
6-nitro BIPS is one of the most popular Spiropyrans

BISO

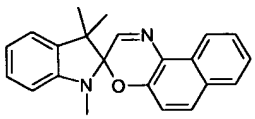


Benzo Indolino Spiro Oxazine

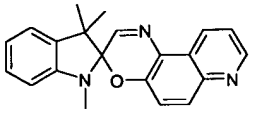
BR bacteriorhodopsin
DHI spirodihydroindolizines
DHPP dihydropyrazolo-pyridine
DNE dinaphthylethylene
DPB 1,4-diphenylbuta-1,3-diene
DPH 1,6-diphenylhexa-1,3,5-triene
DPO 1,8-diphenylocta-1,3,5,7-tetraene
HR halorhodopsin
MC merocyanine (open form of SP, SO, etc.)



quinonic form zwitterionic form

NISO  Naphthaleno Indolino SO

NPE naphthylphenylethylene
P_r phytochrome ("red" absorbing)
P_{fr} phytochrome ("far red" absorbing)

QISO  Quinolenyl Indolino SO

SO spirooxazines (such as BISO, NISO, QISO, etc.)
SP spiropyrans

X. TECHNICAL VOCABULARY FOR OPHTHALMIC LENSES

X.1 Luminous transmittance

The darkening efficiency is given by the transmittance variation at a given temperature.

X.2 Activation time

Activation time is the time necessary to achieve a given luminous transmittance by exposure to UV at a given temperature.

X.3 Thermal fade time

Thermal fade (also termed fade-back) time is the time necessary to bleach (indoors) a colored form to one half its original absorbance at a given temperature.

X.4 Bleached state

Bleached state is the colorless form of a photochromic system.

X.5 Activated state

Activated state is the colored form of a photochromic system.

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